

APPLICATION FOR
UNITED STATES PATENT

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for

INFILTRATED ALUMINUM PREFORMS

CERTIFICATION UNDER 37 CFR § 1.10

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Docket No. USA.301-1

INFILTRATED ALUMINUM PREFORMS**CROSS REFERENCE TO RELATED APPLICATION(S)**

5 [0001] This patent application is a continuation-in-part of United States Patent Application Serial Number 10/260,158 for "Infiltrated Aluminum Preforms" that was filed on September 27, 2002. US 10/260,158 is incorporated by reference in its entirety herein.

U.S. GOVERNMENT RIGHTS

10 [0002] Not Applicable

BACKGROUND OF THE INVENTION

1. Field of the Invention:

15 [0003] This invention relates generally to a method for the rapid manufacture of aluminum alloy components and can have specific application to limited production runs, such as those encountered in rapid prototyping or rapid manufacturing. More particularly it relates to a method whereby a porous aluminum or first aluminum alloy preform is formed into a desired shape and supported by a polymeric binder. A second aluminum alloy is caused to infiltrate the porous preform forming a dense structurally sound component.

20 2. Description of the Related Art:

25 [0004] Aluminum and aluminum alloy components are traditionally fabricated by casting, mechanical working or machining, as well as combinations of these processes. When casting, molten metal fills a mould having an internal cavity formed into the shape of a desired component. After the molten metal cools and solidifies, the component is removed from the mould in either net shape (finished form) or near net shape (close to finished form, but requiring some additional working or machining). When mechanical working, such as forging, drawing, rolling, extrusion or stamping, a cast billet of the metal is mechanically deformed into the shape of the desired component. Casting requires moulds machined to the shape of the desired component while tools used to apply mechanical deformation require dies formed to the required shape. While both casting and mechanical working are well suited for the economical manufacture of large quantities of identically shaped components, neither is particularly suitable for specialty applications or prototypes where only a few components are required or where various aspects of the shape are to be varied from component to component.

35 [0005] Aluminum and aluminum alloy components can also be machined from stock material that may have been mechanically worked or cast. Machining is time consuming, has a

very poor utilization of raw material and requires skilled operators. Machined components are therefore expensive and slow to produce.

[0006] Aluminum powders can also be used to fabricate parts, either to take advantage of a unique property set or because net shape parts can be inexpensively fabricated. In the former case, the powders are typically consolidated by extrusion, forging or hot isostatic pressing. Net shape parts are made by pressing aluminum powder at extremely high pressures (nominally in excess of 30,000 pounds per square inch) into hard tooling cavities to achieve green densities as high as 95%. After pressing, the part is ejected from the die and the so-called green body is sintered in a furnace at elevated temperatures under a controlled atmosphere, commonly nitrogen. Aluminum, and aluminum alloys, have a propensity to form a highly stable alumina (Al_2O_3) surface film that passivates the individual powder particles limiting further oxidation. The surface oxide also hinders the diffusional mechanisms needed to sinter aluminum powder preforms into fully dense aluminum components. As a solution to this challenge, the aluminum powder industry has developed blends of aluminum powder, surface oxide reducing agents, lubricants and sintering agents. All of these technologies require tooling or dies which are used to shape the part. This tooling is expensive and is time consuming to produce. This delays the time needed to introduce new products and increases their cost.

[0007] An alternative production strategy produces three-dimensional objects directly from the manipulation of data from computer aided design (CAD) databases. Various technologies are known to produce such parts, particularly through the use of additive processes as opposed to subtractive processes such as conventional machining. Important additive processes for the production of such parts include stereolithography, selective laser sintering, laminated object manufacturing, three-dimensional printing and fused deposition modeling. A common feature of all of these rapid prototyping and rapid manufacturing techniques is that energy and/or material is delivered to a point to produce a solid. A series of lines are then traced out to make a cross-sectional layer and a series of layers formed to make a three dimensional part. In principle, there are as many such potential manufacturing systems as there are ways to write or draw on a surface. Producing components in this way has a number of important advantages over traditional manufacturing processes. Most importantly, parts of any shape can be produced directly from a CAD model without the need for expensive tooling or machining and these can be produced in a small fraction of the time that is typically required of traditional manufacturing operations.

[0008] Selective laser sintering is described in more detail in US Patent No. 4,863,538 to Deckard and three-dimensional printing is described in more detail in US Patent No. 6,416,850 to Bredt, et al. Both the 4,863,538 patent and the 6,416,850 patent are incorporated by reference in their entirety herein. These techniques have been used to fabricate objects made from a variety of materials such as photoset resins, other polymers such as nylon and ethylene butadiene styrene, organic waxes, ceramics such as SiN, and metals, most commonly steel.

[0009] Recently, aluminum parts have been produced by selective laser sintering and extrusion freeform fabrication. These aluminum parts were fabricated as polymer/aluminum powder composites and post-processed by burning out the polymer and then sintering the remnant metal powder to full or near-full density, in a manner similar to that used in powder injection molding. However, it is extremely difficult to maintain dimensional accuracy during sintering of such a powder preform because of density gradients in the green part and geometrical constraints. While uniform shrinkage can be incorporated into the initial CAD design, non-uniform shrinkage, or distortion, is more difficult to control reproducibly and to accommodate by design. Because dimensional accuracy is a critical criterion for any rapid prototyping/rapid manufacturing system, the inability to accurately sinter large parts is fatal. Only small aluminum parts can presently be made this way: the limit is approximately 1 cm³.

[0010] US Patent No. 4,828,008 discloses that a permeable ceramic mass is spontaneously infiltrated by a molten aluminum alloy containing at least 1%, by weight, of magnesium and optionally also containing silicon. "Spontaneous infiltration" means that the molten metal infiltrates the permeable mass without the requirement for the application of pressure or vacuum (whether externally applied or internally created). US Patent No. 4,828,008 is incorporated by reference in its entirety herein.

[0011] US patent No. 5,020,584 discloses that spontaneous infiltration of a preform formed from a mixture of a powdered matrix metal and a powder filler (ceramic) with a molten metal. It is disclosed that when the powdered matrix metal is aluminum and the filler aluminum oxide, the infiltrating atmosphere forms a skin (such as an oxide or nitrogen compound) on the metal that prevents particle separation. US Patent No. 5,020,584 is incorporated by reference in its entirety herein.

[0012] The dimensional accuracy of a component formed is much improved by infiltration, whether spontaneous, pressure-assisted or vacuum-assisted. The loosely formed powder body is lightly pre-sintered and the porous mass is subsequently infiltrated by a liquid metal at a temperature between the melting point of the infiltrant and the base metal. Because

there is so little sintering, there is negligible dimensional change between the preform and the finished part. Numerous systems have been fabricated by the rapid prototyping/rapid manufacturing/infiltration route to date, including Fe-Cu, stainless steel-bronze, ZrB₂-Cu and SiC-Mg. Aluminum and aluminum base alloys are a conspicuous omission from the successful metallic infiltration systems. It is theorized that the alumina surface film on the aluminum and aluminum alloy particles may have prevented the infiltration of porous aluminum components.

[0013] There remains, firstly, a need for a method to spontaneously infiltrate a porous mass of a first aluminum-base material with a molten second aluminum-base material. In addition, there remains a need for an additive process to manufacture aluminum alloy parts that does not have the above-stated deficiencies. The additive process should result in parts with a density close to the theoretical density of the aluminum alloy and be capable of a high level of dimensional accuracy.

BRIEF SUMMARY OF THE INVENTION

[0014] In accordance with a first embodiment of the invention, there is provided a method for the spontaneous infiltration of a porous aluminum-base preform. This method includes the steps of forming a mixture that contains a binder and at least one of aluminum or a first aluminum-base alloy into a green composite, removing the binder from the green composite forming a porous preform structure, converting a portion of the aluminum to a rigid and continuous aluminum nitride skeleton and infiltrating the porous preform structure with a molten second aluminum base alloy to form the three-dimensional object with near theoretical density.

[0015] In accordance with a second embodiment of the invention, there is provided a method for the manufacture of a three-dimensional object that includes the steps of forming a mixture that contains a binder and at least one of aluminum or a first aluminum-base alloy into a green composite, removing the binder from the green composite forming a porous preform structure, converting a portion of the aluminum to a rigid and continuous aluminum nitride skeleton and infiltrating the porous preform structure with a molten second aluminum base alloy to form the three-dimensional object with near theoretical density.

[0016] The green composite may be formed by an additive process such as computer aided rapid prototyping, for example selective laser sintering or a casting or molding process such as a room temperature vulcanization process like the Keltool® process, metal injection molding, extrusion molding, resin transfer molding, rotational molding, or pressing. The

method facilitates the manufacture of small numbers of aluminum components by an inexpensive technique that provides high dimensional stability and high density.

[0017] For either the first embodiment or the second embodiment, a continuous aluminum nitride skeleton is formed on the surfaces of the aluminum particles or the particles of a first aluminum-base alloy powder for increased preform strength and dimensional stability. It is a feature of the invention that enhanced infiltration may be achieved by utilizing a nitrogen based atmosphere for the converting step and a noble gas based atmosphere, such as argon, for the infiltrating step. Using a noble gas based atmosphere for the infiltrating step improves surface finish, broadens the range of possible infiltrants that can be used and increases mechanical properties. It is a further feature of the invention that infiltration can be achieved by infiltrating at a temperature in excess of the melting point of the aluminum or first aluminum based alloy used to make the green composite.

[0018] The details of one or more embodiments of the invention are set forth in the accompanying drawings and the description below. Other features, objects and advantages of the invention will be apparent from the description and drawings, and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 1 shows in flow chart representation a process for the infiltration of a porous aluminum-base preform by a molten aluminum-base alloy.

[0020] FIG. 2 graphically illustrates the effect of nitride skin thickness on tensile ductility of the composite.

[0021] FIG. 3 graphically illustrates the rate of nitride formation as a function of both temperature and the presence of tin.

[0022] FIG. 4 graphically illustrates the rate of nitride formation as a function of tin content.

[0023] FIG. 5 graphically illustrates the effect of tin on the infiltration rate.

[0024] FIG. 6 shows in cross-sectional representation an aluminum alloy particle used to form the porous mass in accordance with an embodiment of the invention.

[0025] Fig. 7 shows in cross-sectional representation a blend of powders in accordance with an embodiment of the invention.

[0026] Fig. 8 shows in cross-sectional representation the effect of initial heating on the blend of powders shown in Fig. 3.

[0027] Fig. 9 shows in cross-sectional representation the effect of nitridation on the blend of powders shown in Fig. 3.

[0028] Like reference numbers and designations in the various drawings indicated like elements.

DETAILED DESCRIPTION

[0029] Figure 1 shows in flow chart representation a sequence of process steps 10 in accordance with a first embodiment of the invention. In a first step 12, a mixture containing a binder and at least one of aluminum or a first aluminum-base alloy is formed into a green composite. As used herein, "aluminum-base" means that the alloy contains at least 50%, by weight, of aluminum.

[0030] Preferably the mixture comprises a minimum of three powders blended together. One powder is an aluminum alloy, such as aluminum alloy 6061, that constitutes approximately about 80 to about 95%, by volume, and more preferably from about 85% to about 90%, by volume, of the total mixture. This base metal may be any aluminum-base alloy powder or pure aluminum.

[0031] The aluminum or first aluminum-base alloy is in powder form of any effective particle size. Preferably the average particle size is between about 5 and about 150 microns (1 micron = $1\ \mu\text{m} = 1 \times 10^{-6}$ meter) and more preferably, the average particle size of the metallic powder is in the range of from about 10 to about 75 microns. One preferred aluminum alloy is aluminum alloy 6061 that has a nominal composition, by weight, of about 0.4% to about 0.8% silicon, about 0.15% to about 0.40% copper, about 0.8% to about 1.2% magnesium, about 0.04% to about 0.35% chromium and the balance aluminum and unavoidable impurities.

[0032] As a non-limiting list, the aluminum may be alloyed with one or more of the following elements tin, lead, bismuth, indium, copper, magnesium, silicon, zinc, titanium, chromium, zirconium, nickel, iron, manganese and silver.

[0033] Tin is preferred as an alloying addition because tin improves the wetting of the infiltrating liquid and controls the nitride growth rate. The amount of nitride that forms is a critical parameter that controls both infiltration and properties of the finished product. If insufficient nitride forms, then dimensional stability is compromised during infiltration. Excess nitride detrimentally impacts the mechanical properties, such as tensile ductility. With reference to Figure 2, the weight gain of an aluminum-2% magnesium – 1% silicon preform that is infiltrated with aluminum-5% magnesium is assumed due to the formation of nitride. As the weight increases, the tensile ductility decreases. Excess nitride can also cause cracking that can limit the production of large parts.

[0034] Because nitride growth is important, rapid nitride growth rates make the process difficult to control by decreasing the size of the operational window and increasing

costs. An addition of tin facilitates control of the nitride growth. With reference to Figure 3, the amount of nitride that forms and the rate at which the nitride grows are dependent on the reaction time and temperature. Without tin at either 540°C or 570°C, the initial rate is
5 reasonably slow, however the rate of nitride formation accelerates after approximately four hours. With tin, the rate of growth does not change over time and therefore the amount of nitride that forms in a given time is less when tin is added to the powder mixture than when it is not.

[0035] The effect of tin concentration on the weight gain due to nitridation is shown in
10 Figure 4. A tin content as low as 0.1%, by weight, is effective and a content of between 0.5% and 1.0%, by weight, is preferred.

[0036] With reference to Figure 5, the tin also affects the infiltration rate. Without tin, there is an incubation period. This incubation period is reduced in the presence of tin. The maximum infiltration rate is also greater in the presence of tin than without any tin present.

15 [0037] Tin powder may be mixed with the aluminum powder or prealloyed into the aluminum powder. Either embodiment is effective to control nitride growth rate. Prealloying tends to reduce variability in tensile properties, presumably because there is less segregation than when powders are mixed.

[0038] Other alloying additions also affect the growth of the nitride skeleton. In the
20 absence of tin, the nitride formation rate is highest for pure aluminum and lower for aluminum containing additions of silicon and magnesium, referred to as aluminum alloys of the 6xxx series, where x is between 0 and 9.

[0039] In addition to aluminum alloy 6061, the following aluminum alloys have been shown to reduce the rate of nitride formation and are examples of the preferred first aluminum-
25 base alloy: 6063, nominal composition by weight, Al-0.7% Mg – 0.4% Si; 6082, nominal composition by weight Al-0.9% Mg – 1.0% Si – 0.7% Mn; 6106, nominal composition by weight Al-0.6% Mg – 0.45% Si – 0.25% Cu and 6351 nominal composition by weight Al-0.6% Mg – 1.0% Si – 0.6% Mn. Other aluminum alloys may be used in the presence of tin.

[0040] A second powder component of the mixture, constitutes approximately about
30 0.1 to about 4%, by weight, and preferably from about 1.5% to about 2.5%, by weight of the total mixture. This second powder is an oxygen-scavenger, such as magnesium that cleans the atmosphere surrounding the mixture and reduces the oxide layer on the aluminum-base metal particles. The oxygen scavenger is in particle form with an average particle size of between about 5 and about 150 microns and preferably the average particle size is between about 10 and

about 75 microns. Other suitable oxygen scavengers include zirconium, lithium, beryllium, calcium, cerium, lanthanum, neodymium, praseodymium, samarium, thorium, uranium, or misch metal or aluminum alloyed with magnesium, zirconium, lithium, beryllium, calcium, cerium, lanthanum, neodymium, praseodymium, samarium, thorium, uranium, or misch metal.

[0041] As disclosed hereinbelow, while there are benefits to including the oxygen scavenger in the powder mixture, effective infiltration is also obtained if the oxygen scavenger is included in a support layer formed about the green composite, in which case the oxygen scavenger may be omitted from the powder mixture.

[0042] A third powder component of the mixture, which constitutes approximately 5-15%, by volume, and preferably about 8% to about 12%, by volume, of the total blend, includes a binder. The binder may be an organo-metallic binder such as zinc stearate, an organic or an inorganic binder, but preferably is an organic polymeric binder. Organic polymeric binders can include thermoplastics with sharp melting points such as nylon 6, nylon 11, nylon 12, copolymers of nylon 12 and nylon 6, polyacetals, polyethylene, polyethylene copolymers, polymethacrylates, polypropylene, and polyether block amides. The average particle size of the polymer binder powder is generally in the range of about 1 to about 50 μm . The binder is selected to be a material that decomposes to a gas with a minimum of carbon residue when heated to a temperature of between about 300°C and about 500°C in a suitable atmosphere, such as nitrogen. Where nitrogen is used to create the atmosphere, the nitrogen source can be pure nitrogen, a mixture of gases including nitrogen or any nitrogen rich material that evolves nitrogen to form a nitride skeleton.

[0043] The green composite is heated relatively slowly, such as about 1 to about 2°C per minute to facilitate binder vapor outgassing from the green composite by way of open, connected, porosity without a build up of localized pockets of vapor pressure that could damage the part. Preferred binders have a relatively low melt flow viscosity (on the order of 25 to 145 grams per 10 minutes) and substantially complete decomposition to nitrogen, nitrogen compounds and other gases when heated to a temperature in the 300°-500°C range. Suitable binders include the aforementioned nylons, and more specifically Orgasol® 2001 Nylon-12 (gram molecular weight of 17,400, melt flow viscosity of about 25 to about 100 grams per 10 minutes and decomposition temperature of about 433 to about 481°C), Orgasol® 3501EXD (gram molecular weight of 6,500, melt flow viscosity of about 25 to about 100 grams per 10 minutes and decomposition temperature of about 414 to about 472°C) and Orgasol® 3501UD (melt flow viscosity of about 25 to about 100 grams per 10 minutes and

decomposition temperature of about 425 to about 472°C). All of these aforementioned Orgasol® nylon binders are available commercially from Atofina SA, of 4-8, cours Michelet - La Défense 10 – F-92800 Puteaux – France.

5 [0044] A homogeneous green composite of the powders having a desired shape is formed either by deposition in a mould or by using any rapid prototyping technique, such as those described above. A resin-bonded preform is formed by exposing the green composite to a suitable cure initiator, such as heat or ultra-violet light. This resin-bonded preform has a density of approximately about 40% to about 70% of the theoretical density for the aluminum
10 alloy and structurally has an interconnecting network of pores extending through the preform.

 [0045] The binder is next removed, as illustrated in Fig. 1 by numeral 14, such as by thermal decomposition, by heating to a temperature in the range of from about 300°C to about 500°C with a sufficiently low heat up rate to avoid the formation of high pressure vapor pockets. Removal of the polymer binder will temporarily reduce the integral strength of the
15 part. To provide support, a support powder that will not bond to the part under the processing conditions surrounds the preform. Suitable support powders include ceramics, such as alumina, silicon carbide and boron nitride, mixed with an oxygen scavenger, such as magnesium. As noted above, inclusion of an oxygen scavenger in the support powder may be sufficiently effective to remove the need to include an oxygen scavenger in the mixture of
20 powders forming the green composite.

 [0046] The oxygen scavenger is present in an amount of from about 0.1% to about 10%, by volume, of the support powder, and more preferably, is present in an amount of from about 0.5% to about 5%, by volume. A preferred scavenger is magnesium powder. The magnesium forms an oxygen scavenging blanket that envelopes the component, reducing the
25 oxygen content within the part to negligible levels. Other metal powders that may be mixed with the ceramic support powder are titanium, zirconium, lithium, beryllium, calcium, cerium, lanthanum, neodymium, praseodymium, samarium, thorium, uranium, or misch metal and mixtures thereof, either in combination with magnesium, as a substitute for magnesium or in combination with aluminum.

30 [0047] Once the binder has been removed, the temperature is increased to a temperature, effective to promote the formation of aluminum nitride at low oxygen partial pressures. An aluminum nitride skeleton forms on the surface of the aluminum-base alloy powders. The aluminum nitride skeleton is rigid and continuous and significantly increases the strength of the composite. However, because the skeleton is also rigid, an excessively thick

skeleton is not desirable due to the resultant decreased ductility. Since the rigid skeleton provides dimensional stability, it should not be attacked by the liquid infiltrate.

[0048] A suitable thermal profile includes at least two isothermal holds. The first isothermal hold occurs at a temperature of between 500°C and 570°C for a time of from 2 to 20 hours. A preferred first isothermal hold is 540°C for from six to 12 hours. The second isothermal hold is at a temperature above the melting temperature of the infiltrant initiating infiltration 16. Nitridation 15 continues during the first hold and an initial portion of the second isothermal hold and only stops when liquid infiltrant covers the exposed surfaces of the component.

[0049] A second suitable thermal profile is particularly effective to prevent a rough surface on the component that has been compared to an orange peel appearance. The orange peel effect is most prevalent on parts having large, flat, surfaces and is believed due to surface porosity and incomplete infiltration. The surface finish is improved when the process gas is changed from nitrogen to a noble gas after the first isothermal hold. Changing the gases stops nitridation 15 and eliminates the orange peel effect. In accordance with this profile, the first isothermal hold is as above, at a temperature of between 500°C and 570°C for a time of from 2 to 20 hours and preferably at 540°C for from six to 12 hours. Once nitridation 15 is complete, the process gas is changed to a noble gas, such as argon, helium or neon, and the system is purged under the noble gas for an effective amount of time, such as about one hour. Argon is preferred as the noble gas. The temperature is then increased to the second isothermal hold which is at a temperature above the melting point of the infiltrant, held at temperature until infiltration 16 is completed and then cooled to room temperature (nominally 22°C).

[0050] The infiltrant is selected to melt at a temperature higher than that required for skeleton formation. For the successful infiltration of a freestanding part (i.e. one not confined within a mould), it is necessary to form a rigid and inert skeleton as this enables shape retention during infiltration by the liquid. While it was originally presumed that the infiltrant must melt at a temperature less than the melting point of the base alloy or dimensional stability would be lost, it is now recognized that the AlN skeleton, having a melting point of about 3000°C, remains solid at any practical infiltration temperature and maintains the shape of the component. The melting point of the infiltrant is therefore not important, as long as the infiltrant melts at a temperature above that which the AlN forms. By melt, it is meant the temperature at which a liquid phase initially forms, referred to by those skilled in the art as the solidus temperature.

[0051] In addition, the infiltrant must have sufficient fluidity and a sufficiently low viscosity to flow through the interconnected pores of the composite. In addition, the contact angle between a bead of the infiltrant and the skeleton must be sufficiently low to support good wetability. A contact angle of greater than 90° is typically viewed as non-wetting while a contact angle of less than 90° is viewed as wetting, with the closer to 0° the more effective the infiltration. Further considerations are the solubility of the aluminum alloy powder in the liquid infiltrant and the phase diagram of the combination of aluminum alloy powder and infiltrant. A large number of phases or a number of transient phases is not desirable, since that could lead to inhomogeneity in the solidified composite.

[0052] The infiltrant may be aluminum or an aluminum based alloy further containing, as a non-limiting list, one or more of the following: copper, magnesium, silicon, zinc, titanium, zirconium, manganese, chromium, iron, silver, lead, tin, bismuth, antimony, strontium, sodium and nickel.

[0053] As a non-exclusive list, the following alloys are useful as the infiltrant. All compositions are specified in weight percent. Each composition may contain other, unspecified elements in amounts that do not materially affect the infiltration properties described above.

[0054] Silicon 8%-18%

Magnesium 3% - 7%

Aluminum balance.

Nominal (Al-13.8% Si – 4.7% Mg) melting temperature of 557°C.

[0055] Copper 28% - 38%

Aluminum balance.

Nominal (Al – 33% Cu) melting temperature of 548.2°C.

[0056] Silicon 8% - 12%

Zinc 8% - 12%

Nickel 3% - 8%

Aluminum balance.

Nominal (Al-10.5% Si – 10% Zn – 5.5% Ni) melting temperature of 549°C.

[0057] Silicon 8% - 18%

Aluminum balance.

Nominal (Al-12% Si) melting temperature of $577 \pm 1^\circ\text{C}$.

- 5 [0058] Other suitable infiltrants are listed in Table 1. Each composition may contain other, unspecified elements in amounts that do not materially affect the infiltration properties described above.

Table 1

Infiltrant (Alloying Additions in Weight Percent, Balance Aluminum)	Solidus ($^\circ\text{C}$)	Liquidus ($^\circ\text{C}$)	Range ($^\circ\text{C}$)
Al - 2.4 Zn	650	656	6
Al - 2.9 Fe	654	660	6
Al - 2.2 Zn	639	653	14
Al - 2.7 Mn	658	677	19
Al - 2.3 Cu	604	654	50
Al - 5 Mg	580	635	55
Al - 2 Cu - 1 Mg	584	650	66
Al - 1 Si - 0.9 Mg - 0.7 Mn	580	649	69
Al - 2.3 Si	577	647	70

- 10 [0059] Once at the infiltration temperature, generally at least about 10°C above the melting temperature of the infiltrant, the part is held at temperature for a time effective for complete infiltration 16 of molten infiltrant into the preform, on the order of about 0.5 to about 15 hours, and preferably from about 1 hour to about 10 hours. At which time the part is cooled, typically at a rate of from about 1°C per minute to about 5°C per minute, and
15 nominally $2^\circ\text{C}/\text{minute}$, to solidify 18.

- [0060] Following solidification, the strength of the part may be increased by heat treating the infiltrated part. One suitable heat treatment is to heat to from about 500°C to about 550°C for from about 1 hour to about 24 hours followed by a water quench. Additional strength is achieved through age hardening, either at room temperature (natural aging) or at
20 elevated temperatures, typically at about 100°C to about 200°C , for a time effective to promote full hardening.

[0061] Other post-solidification treatments may include hot isostatic pressing to close residual porosity and polishing or sand blasting to provide a smooth finish to the part.

[0062] The mechanism by which the Applicants successfully spontaneously infiltrated an aluminum alloy with a different aluminum alloy is believed to be the following. This represents Applicants best understanding of the process as of the filing of the patent application. With reference to Fig. 6, a particle of aluminum alloy powder 20 has a metallic core 22, such as, by weight, nominally Al-1% Mg – 0.6% Si-0.25% Cu for aluminum alloy 6061. Surrounding the core 22 is a thin, chemically and thermally stable, alumina film 24.

With reference to Fig. 7, a blended mixture of powders 26 is formed. The mixture 26 includes aluminum or aluminum alloy particles 20 (the alumina film is present, but sufficiently thin not to be illustrated in Fig. 7), oxygen scavenger particles 28, such as magnesium, and a polymer binder 30, such as nylon-12. As nominal quantities, there is about 2%, by weight of the oxygen scavenger and about 10% by volume of the binder with the balance aluminum alloy particles.

[0063] With reference to Fig. 8, the blend of powders of Fig. 7 is formed into a desired near net shape, such as by rapid prototyping and optionally surrounded by a support layer, such as a mixture of alumina and magnesium powders (not shown). A desired infiltrant 32, such as, by weight, nominally Al-13.8% Si – 4.7% Mg, is placed in contact with the blend of powders.

The assembly 34 is then heated in an inert atmosphere, preferably nitrogen containing and more preferably, substantially only nitrogen to a temperature effective to melt the polymer binder 30, without melting any of the metallic components (aluminum alloy powder 20, oxygen scavenger 28 and infiltrant 32). For a nylon-12 binder, this temperature is in the range from about 150°C to about 300°C. As the blend of powders is further heated, such as through the temperature range of from about 300°C to about 540°C in nitrogen, the polymer binder 30 begins to decompose. If the polymer binder 30 is nylon-12, the binder decomposes to a carbonaceous residue, ϵ -Caprolactam ($C_6H_{11}NO$) and gaseous fixed nitrogen species such as HCN, N_2O and NH_3 . Gaseous carbon species such as CO and CO_2 are also formed.

[0064] While the assembly may be moved to different ovens to achieve the desired thermal exposures, it is preferred that the assembly remain in a single atmosphere controlled oven programmed with temperatures and time periods sufficient to perform each process step in series.

[0065] With reference to Figure 9, after the removal of the binder, the part is held at a temperature between the lowest temperature at which the aluminum nitride compound forms

and the temperature at which infiltration occurs in a nitrogen-containing atmosphere.

Preferably, the atmosphere is substantially only nitrogen. By applying an isothermal hold in this temperature band, and providing the oxygen content is sufficiently low, partial conversion of the aluminum to an aluminum nitride compound 36 occurs. Growth of the aluminum nitride compound in a continuous network results in the formation of a rigid skeleton. The hold time should be such as to allow sufficient but not excessive formation of this skeleton. Typically, a hold time of about 2 hours at about 540°C is used. Once a skeleton has formed, the atmosphere is changed from nitrogen to argon and the temperature is then increased to above that at which the infiltrant 32 becomes molten to allow spontaneous or pressureless infiltration of the part. The part is held at the infiltration temperature sufficiently long to ensure full penetration of the liquid, typically about 1 hour to about 10 hours.

[0066] The above invention will become more apparent from the Examples that follow.

EXAMPLES

Example 1

[0067] A green composite was made by selective laser sintering of a powder mixture containing 6061 powder, 2 wt% Mg and 10-vol% nylon binder using each of the nylon binders previously recited as being commercially available from Atofina S.A. An infiltrant with a composition, by weight, of Al-13.8Si-4.9Mg was placed in contact with the preform. The amount of the infiltrant was sufficient to just fill the pore volume. The assembly was then placed inside a crucible and covered with a support powder consisting of alumina containing 1 vol % Mg powder. The crucible was then placed inside a nitrogen-atmosphere furnace and heated at approximately 90°C per hour to a temperature of 540°C and held for a period of 2 hours to allow the skeleton to form. The furnace temperature was then increased at the same rate to 570°C and held for 4 hours to allow spontaneous infiltration of the whole preform. The parts were then furnace cooled until the temperature was below 200°C and then removed from the furnace and air-cooled. The parts were removed from the support powder and sand blasted. The density of each part was close to the theoretical density for the aluminum-base alloy.

[0068] Similarly successful infiltrations were obtained by the processes recited in Examples 2 through 7 that follow.

Example 2

[0069] An alloy was made and processed as per Example 1 but with an infiltrant
5 composition of Al-33wt% Cu.

Example 3

[0070] An alloy was made and processed as per Example 1, but with an infiltrant
composition of Al-10.5Si-10Zn-5.5Ni.

10

Example 4

[0071] An alloy was made and processed as per Example 1, but with an infiltrant
composition of Al-12Si and an infiltration temperature of 590°C.

15 **Example 5**

[0072] An alloy was made and processed as per Example 1, but the initial powder
mixture consisted of 6061 powder and 10-vol% nylon binder.

Example 6

20 [0073] An alloy was made and processed as per Example 1, but the initial powder
mixture consisted of aluminum powder, 2 wt% Mg and 10-vol% nylon binder.

Example 7

[0074] A powder mixture containing 6061 powder, 2 wt% Mg and 10 vol% nylon
binder using each of the nylon binders previously recited as being commercially available from
25 Atofina S.A. was made into a cast preform by placing the powder mixture in a mould and
heating this to a temperature above the melting point of the nylon. On cooling, the preform was
extracted from the mould and processed as per Example 1.

Example 8

30 [0075] To confirm the hypothesis that the melting point of the infiltrant could exceed
the melting temperature of the base alloy, cast preforms were made by the method of Example

7 from a mixture of 2%, by weight, magnesium powder, 1% by weight tin powder, balance aluminum alloy 6061 powder combined with 10%, by volume, nylon. The mixture was nitrided for 12 hours at 540°C in nitrogen, purged for one hour in argon and then infiltrated with commercially pure aluminum (99.7%) in argon at 700°C for six hours. Dimensional accuracy was maintained and acceptable parts were produced.

Example 9

[0076] To confirm the hypothesis that the infiltrant may have a relative broad melting range, cast preforms were made by the method of Example 7 from a mixture of aluminum alloy 6061 powder, 2%, by weight magnesium powder, 1%, by weight, tin powder and 10%, by volume, nylon, were nitrided for 12 hours at 540°C in nitrogen, purged for 1 hour in argon and then infiltrated in argon at 700°C for six hours. The samples were then annealed in air for two hours at 410°C and water quenched. When the infiltrant was Al-5%, by weight, Mg (melting range of 55°C), the ultimate tensile strength of the finished part was 155 MPa and the tensile ductility was 1.6%. When the infiltrant was Al-14%, by weight, Si – 4%, by weight, Mg (melting range of 0°C), the ultimate tensile strength of the finished part was 100 MPa and the tensile ductility was 0.5%. When the infiltrant was pure aluminum, the ultimate tensile strength of the finished part was 103 MPa and the tensile ductility was 2%.

[0077] It should be noted that the present process is applicable to other materials and compositions, and one skilled in the art will understand that the alloys, blend percentages, particle sizes, and temperatures described herein are presented as examples and not limitations of the present invention.

[0078] One or more embodiments of the present invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.